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Ni-hydroxide growth in vacuum plasma sprayed electrodes for alkaline electrolysis

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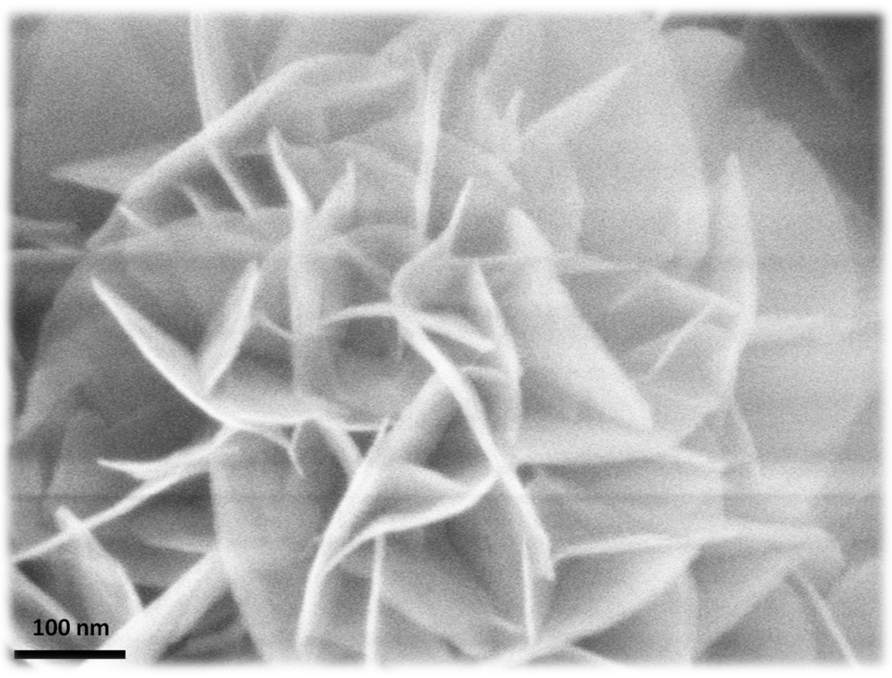
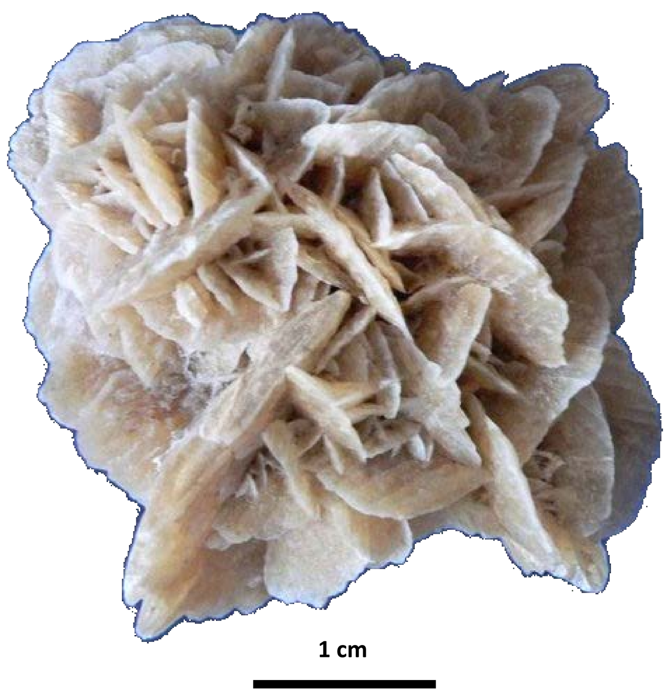
Introduction

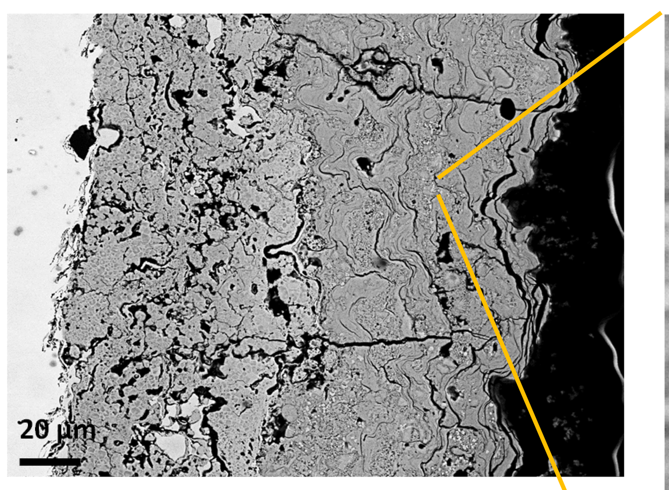


The EU FCH-JU RESelyser project is concerned with the development of high pressure, high efficiency and low cost alkaline water electrolysers that can be operated variably and intermittently to meet the demands for integration into energy networks relying on fluctuating renewable energy. The project utilizes NiAlMo alloy electrodes produced at the German Aerospace Center (DLR) by vacuum plasma spraying (VPS). VPS results in a heterogeneous microstructure consisting of a multitude of intermetallic phase sub domains and pores. Prior to electrolysis operation the electrodes are activated by leaching of Al and some Al containing intermetallic phases leaving micrometer pores and nanometer dendritic pores increasing the surface area available for the electrolysis reactions. Post mortem analysis of the electrodes revealed "desert rose" like nano flakes on the surfaces and in the pores. Earlier microscope analysis of Raney-Nickel electrodes for alkaline electrolysis (Ref. 1, 2, 3) has also reported on very fine unidentified nano structures on electrode surfaces. This study seeks to investigate the nature and the formation of these nano structures.

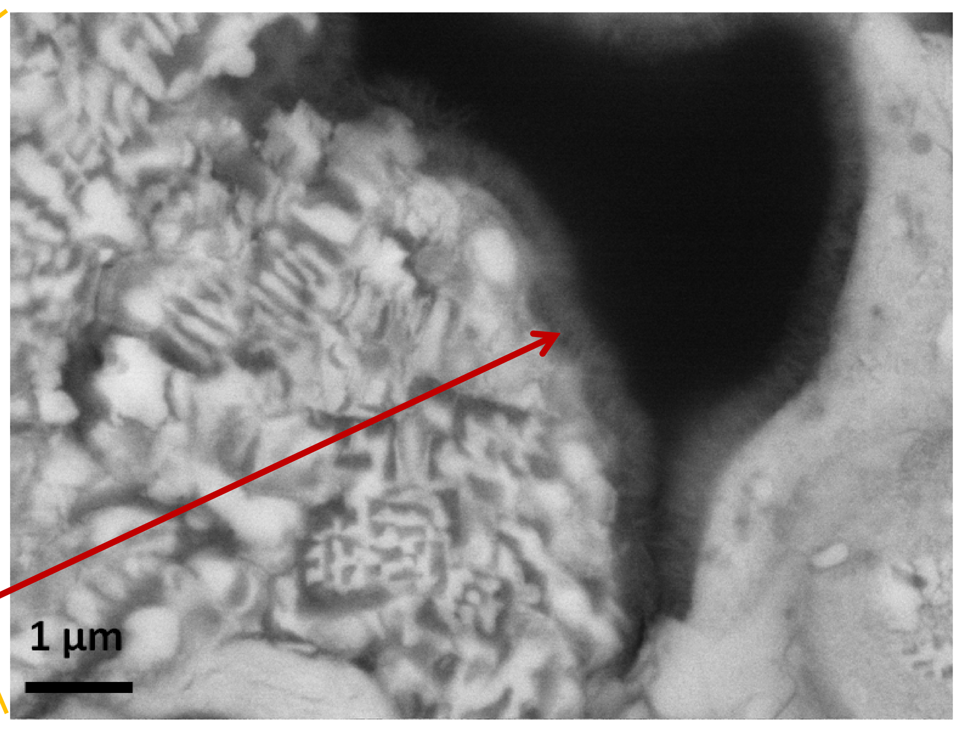


Results and discussion

Analyses of cross sections and electrode surfaces revealed desert rose like nano flake structures on the surfaces and in the pores of several electrodes, depending on the electrode history. The size of the faceted flakes varied from tens of nm to 1-2 µm where the thickness varied from a few nm to ~20 nm. The particles were too fine for reliable EDS analysis in SEM. However, high oxygen and Ni contents were indicated in the flakes. Similarly, the activated NiAlMo powder showed emerging desert rose structure after storage in distilled water.

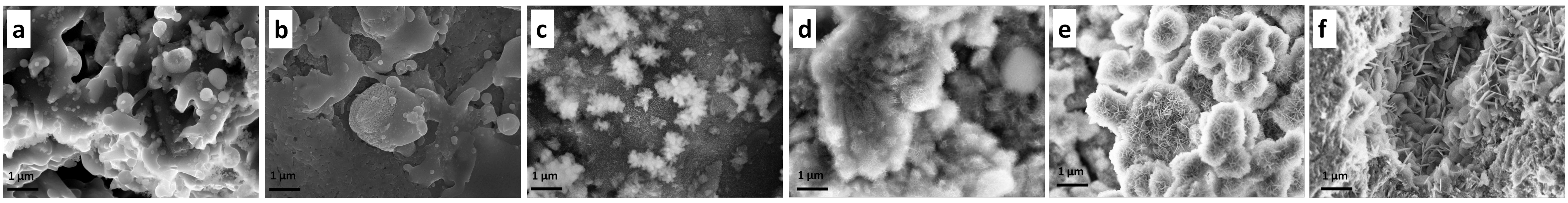


Cross section of NiAlMo electrode showing heterogeneous porous structure and nano particles on the pore surfaces.

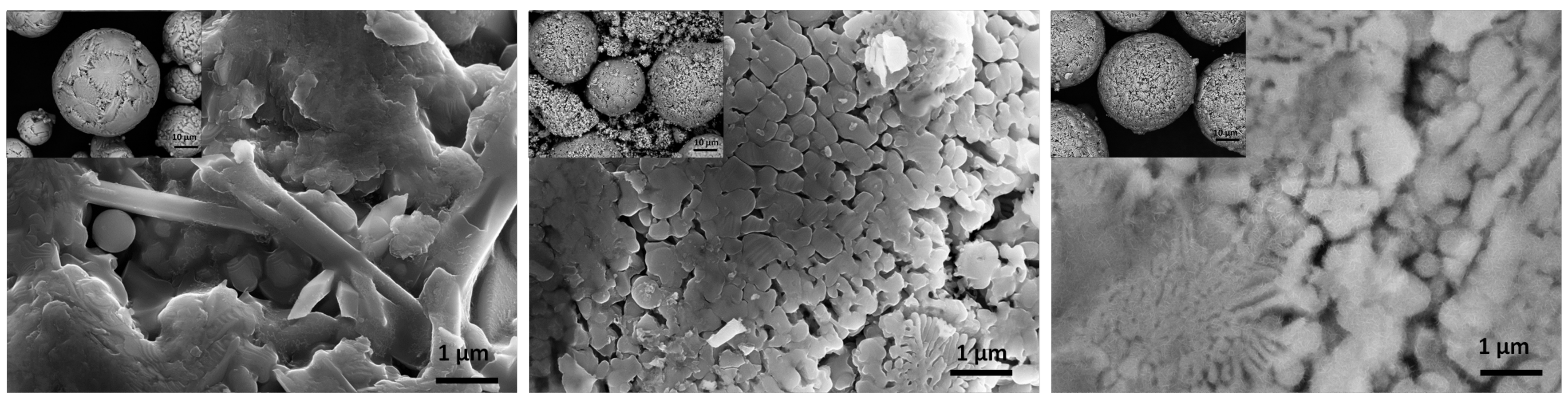


Experimental

Vacuum plasma sprayed NiAlMo alloy electrodes were characterized before and after electrolysis operation and after storage in distilled water for various length of time. For comparison, NiAlMo raw powder for VPS spraying, powder after leaching out Al, and the leached powder stored in distilled water for 40 days were also analyzed. The microstructural investigation was carried out applying a FEGSEM (Zeiss Supra 35) and HRTEM (JEM-3000F) .

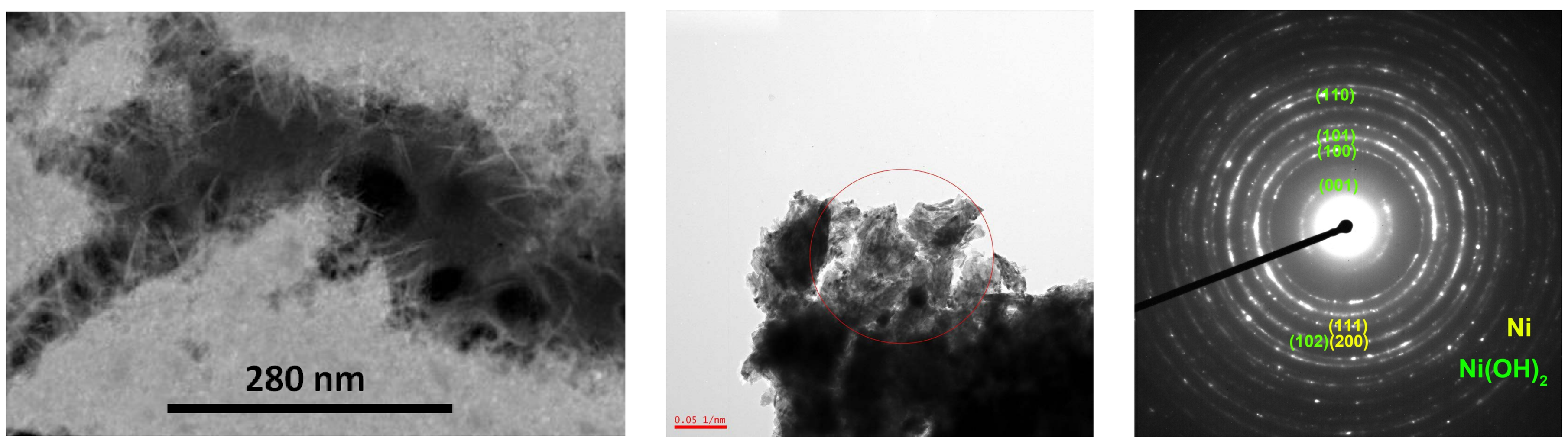


Formation of desert rose nano flakes on the NiAlMo electrode surfaces and in pores as a function of sample history. SEM images of electrode surfaces a) as sprayed; b) leached, washed and dried; c) leached, washed and stored in water 3 days; d) leached, washed and stored in water 210 days.; e) leached, washed, stored 120 days in water, and operated as electrode for ~30 min.; f) leached, washed, stored 90 days in water, and operated as electrode for 28 days..



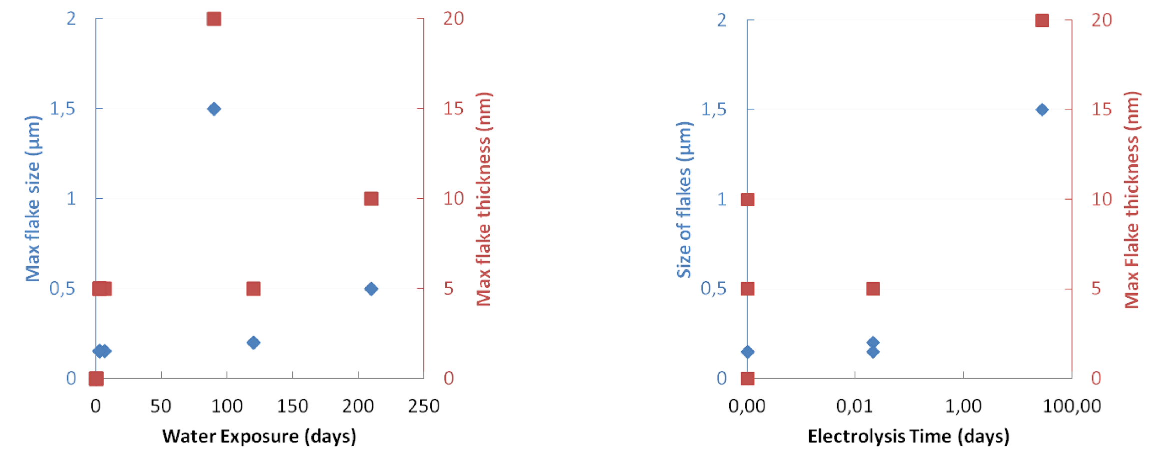
Formation of nano structures on the NiAlMo powders as a function of sample history. Left) NiAlMo raw powder; center) NiAlMo powder leached for Al; right) NiAlMo powder leached, washed and stored in distilled water for 40 days. Insets are powders in smaller magnification.

X-ray diffraction of the surfaces covered with the desert rose structures revealed a very high content of theophrastite , $Ni(OH)_2$ (hexagonal (a=3.126 Å, c=4.605 Å) along with Ni. TEM on a lamella prepared by FIB from a NiAlMo electrode after electrolysis elucidated the desert rose structure in cross-section. The electron diffraction patterns from areas with nano structures in the pores and pieces of scraped off electrode surface after electrolysis could be identified as a mixture of $Ni(OH)_2$ and Ni.



TEM images of areas with nano structures in the pores (left) and of a piece of scraped off (centre) NiAlMo electrode after electrolysis and the corresponding electron diffraction pattern (right).

Evaluation of the flake size of the desert rose structure as function of sample history indicated that the formation of the desert rose structure was related to the electrolysis operation involving exposure to KOH at ~ 70˚C as well as the duration of storage in distilled water at room temperature. Surface area measurements (BET) of scraped off electrodes before and after electrolysis test indicated a factor of approximately three times increase in specific surface area.



Flake size as a function of left) storage time in distilled water; right) electrolysis time.

Conclusion

The desert rose structure on the NiAlMo electrodes for alkaline electrolysis occurred only after storage in water and/or electrolysis operation; not on the as "VPS sprayed" or on as "activated" electrodes. The size of the flakes appeared to be more affected by the time of electrolysis/exposure to KOH at elevated temperature than by the time of storage in water. TEM and XRD studies strongly indicates the desert rose structures to consist of theophrastite, $Ni(OH)_2$. The growth of the flakes is likely to depend on the pH in the storage solution which in turn may depend on washing conditions. The implications, positive or negative, for the application and performance of the electrodes would depend on the electronic and catalytic properties of the precipitates, and whether the precipitation takes place during operation or at breaks in the operation.

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